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<b>(21) International Application Number:</b> PCT/JP96/01781 <b>(22) International Filing Date:</b> 27 June 1996 (27.06.96)  <b>(30) Priority Data:</b> 7/161278                      27 June 1995 (27.06.95)                      JP  <b>(71) Applicant (for all designated States except US):</b> KAO CORPORATION [JP/JP]; 14-10, Nihonbashi-Kayabacho 1-chome, Chuo-ku, Tokyo 103 (JP).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> HASEBE, Keiko [JP/JP]; Kao Corporation, Research Laboratories, 1334, Minato, Wakayama-shi, Wakayama 640 (JP). SUZUKI, Tadayuki [JP/JP]; Kao Corporation, Research Laboratories, 1334, Minato, Wakayama-shi, Wakayama 640 (JP). HIOKI, Yuichi [JP/JP]; Kao Corporation, Research Laboratories, 1334, Minato, Wakayama-shi, Wakayama 640 (JP).  <b>(74) Agents:</b> FURUYA, Kaoru et al.; Nihonbashi TM Building, 1-8-11, Nihonbashi-Horidomecho, Chuo-ku, Tokyo 103 (JP).		<b>(81) Designated States:</b> BR, CN, JP, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> LIQUID COMPOSITION FOR STABILIZING AMINO ACID SERIES HERBICIDES		
<b>(57) Abstract</b>  A liquid enhancer composition for amino acid series herbicides comprising specific tertiary amine and a derivative thereof, at least one oxalic acid or a salt thereof selected from the group consisting of oxalic acid, potassium oxalate, alkanolamine salts of oxalic acid, and lower alkylamine salts of oxalic acid, wherein the ratio of oxalic acid or the salt thereof is 0.1 to 10 times mole per mole of the nitrogen-containing compound. The enhancer composition of the present invention has an excellent stability with lapse of time to a change in temperatures and can markedly enhance the medicinal efficacy of an amino acid series herbicide even when the composition is used in a liquid form in combination with the herbicide.		

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## Description

**LIQUID COMPOSITION FOR STABILIZING AMINO ACID SERIES HERBICIDES**

## [Field of the Invention]

The present invention relates to an enhancer composition for agricultural chemicals and an agricultural chemical composition containing the same, more specifically to a liquid enhancer for herbicides having a higher enhancer effect to amino acid series herbicides, which is represented by glyphosate, and an excellent storage stability.

## [Related Art]

Agricultural chemicals including insecticides, fungicides, herbicides, miticides, and plant growth regulators have been used in the forms of emulsions, wettable powder, granules, powder materials, and flowables. In using them, various attempts in terms of the properties of the formulations have been made in order to fully bring out the effectivenesses of agricultural chemical components. However, the existing situation is that it is difficult to further enhance the effectivenesses of agricultural chemicals through contrivances in terms of formulations. It is

further difficult to develop novel agricultural chemicals, so that it is industrially very significant to further enhance the activities of existing agricultural chemicals.

As substances having the effect of enhancing the activities of agricultural chemicals, surfactants comprising various nitrogen-containing compounds such as quaternary ammonium salts, betaines, and amine oxides have so far been known (JP-A-63-145205). It is known as well that among them, quaternized or further polyoxyethylenated long-chain amines are particularly effective (JP-A-4-211002, JP-A-2-295907, and JP-A-63-284106). However, the medicinal efficacy-enhancing effects of these compounds are not necessarily satisfactory, and a further improvement in the effect has been desired. Accordingly, in order to meet such the desire, the present inventors have proposed to use quaternary ammonium salts or tertiary amines or salts thereof in combination with chelating agents, as shown in W095/17817 published in English on July 6, 1995 corresponding to Japanese Patent Application No. 5-337502 filed on December 28,

1993. In addition, WO92/12637 published August 6, 1992 discloses a composition comprising glyphosate, an acid acceptor and a surfactant.

However, further investigations have resulted in clarifying that while this enhancer for agricultural chemicals shows marked enhancer effect to various agricultural chemicals, it is inferior in storage stability, particularly stability to a change in temperatures when it is stored in a liquid form over a long period of time. It has been clarified that this problem is serious particularly when using it in combination with amino acid series herbicides and the medicinal efficacies of amino acid series herbicides can not sufficiently be enhanced in some cases. Accordingly, it has become clear that such problems as described above have to be further improved.

[Disclosure of the Invention]

Intensive researches made by the present inventors in order to obtain an enhancer for amino acid series herbicides which has a good stability to a change in temperatures even when it is stored in a liquid form over an extended period of time have resulted in finding that the intended liquid enhancer

and liquid herbicide composition can be obtained by using a nitrogen-containing compound comprising specific tertiary amine and derivatives thereof in combination with oxalic acid or a specific oxalic acid salt, and thus completing the present invention.

That is, the present invention provides a liquid enhancer composition for amino acid series herbicides characterized by containing at least one nitrogen-containing compound selected from tertiary amines represented by the following Formula (1) and derivatives thereof, and at least one oxalic acid or salt thereof selected from the group consisting of oxalic acid, potassium oxalate, alkanolamine salts of oxalic acid, and lower alkylamine salts of oxalic acid, wherein the content of oxalic acid or a salt thereof is 0.1 to 10 times mole per mole of the nitrogen-containing compound described above:



[wherein

R<sup>1</sup>: represents a linear or branched alkyl group having a carbon number of 8 to 30 or a linear or

branched alkenyl group having a carbon number of 8 to 30, and

$R^2$ ,  $R^3$ : may be the same as or different from each other and each represent a linear or branched alkyl group having a carbon number of 1 to 30, a linear or branched alkenyl group having a carbon number of 2 to 30, or  $-(AO)_n-H$  (AO is an oxyalkylene group having a carbon number of 2 to 4, and n is a number of 1 to 30 on the average.)]

The invention provides, in other words, a liquid enhancer composition for herbicides of amino acid compounds which comprises, or consisting essentially of, (1) at least one nitrogen-containing compound as above defined and (2) at least one oxalic acid compound as above defined, optionally further comprising a surfactant.

It is preferable that the derivative is selected from the group consisting of amine salts, quaternized products, betaines and amine oxides of the tertiary amine compound represented by Formula (1).

The composition may be in the form of an aqueous solution thereof, comprising 10 to 30 percent by weight of the nitrogen-containing compound.

An herbicide composition of the invention comprises (i) an effective amount of at least one nitrogen-containing compound as defined above and an effective amount of the oxalic acid compound as defined above and (ii) a herbicide of amino acid compound, a weight ratio of (i) to (ii) ranging from 0.05/1 to 50/1.

The invention moreover provides a method for enhancing the herbicidal effectiveness of (ii) a herbicide of amino acid compound with (i) an effective amount of at least one nitrogen-containing compound as defined above and an effective amount of the oxalic acid compound as defined above.

The tertiary amine which is the nitrogen-containing compound used in the present invention is represented by Formula (1) described above, wherein  $R^1$  in Formula (1) is preferably a linear alkyl group or a linear alkenyl group having a carbon number of 8 to 20, more preferably an alkyl group or alkenyl group having a carbon number of 8 to 20, which is derived from natural oil and fat; when  $R^2$  and  $R^3$  are  $-(AO)_n-H$ , AO is preferably an oxyalkylene group having a carbon number of 2, and n is preferably a



number of 1 to 10 on the average. To describe concretely, preferred examples of the tertiary amine include mono-long-chain alkylamine, for example, bis(2-hydroxyethyl)cocoamine, bis(2-hydroxyethyl)-tallowamine, bis(2-hydroxyethyl)oleylamine, and bis(2-hydroxyethyl)laurylamine. Further, included are polyoxyalkylenated long-chain alkylamine, for example, bis(polyoxyethylene(EOp = 3 to 30))cocoamine, bis(polyoxyethylene(EOp = 3 to 30))tallowamine, bis(polyoxyethylene(EOp = 3 to 30))oleylamine, bis(polyoxyethylene(EOp = 3 to 30))laurylamine, bis(polyoxyethylene(EOp = 3 to 30))palmstearylamine, bis(polyoxyethylene(EOp = 3 to 10)•polyoxypropylene-(POp = 3 to 10)]cocoamine, and bis(polyoxyethylene[POp = 3 to 10)•polyoxypropylene(EOp = 3 to 10)]tallowamine. In the compounds described above, EOp represents an average addition mole number of ethylene oxide, and POp represents an average addition mole number of propylene oxide.

In the present invention, derivatives derived from the tertiary amine represented by Formula (1) described above can be used as well. The tertiary

amine derivatives described above include amine salts, quaternized products, betaines, and amine oxides.

The tertiary amine salts include salts of inorganic acids such as hydrochloric acid and sulfuric acid, and salts of organic acids such as acetic acid. In particular, hydrochlorides and acetates are preferred.

The quaternized products of the tertiary amines described above can be obtained by using known quaternizing agents. The quaternizing agents include dialkylsulfuric acids (an alkyl group having a carbon number of 1 to 3) and halogenated alkyl (an alkyl group having a carbon number of 1 to 3, a benzyl group).

Products obtained from the tertiary amines described above are preferred as the quaternized products of the tertiary amines used in the present invention. To describe concretely, included are methyl chloride-quaternized products, benzyl chloride-quaternized products, dimethylsulfuric acid-quaternized products and diethylsulfuric acid quaternized products of the tertiary amines described

above.

Further, the following quaternary ammonium salts are preferred as well:

(A) quaternized long-chain amines

(a) tri-lower alkyl long-chain alkylammonium chloride

(i) trimethylcocoammonium (coco=C<sub>12</sub> to C<sub>15</sub> alkyl) chloride

(ii) trimethyloctadecylammonium chloride

(b) dialkyldi-lower alkylammonium chloride

(i) dimethyldioctadecylammonium chloride

(ii) dimethyldicocoalkylammonium chloride

(B) quaternized polyoxyalkylenated long-chain amines

(a) alkyl di(polyoxyethylene) lower alkylammonium chloride

(i) methylbis(omega-hydroxypoly(oxyethylene)-oleo)ammonium chloride in which polyoxyethylene is derived from 2 to 30 moles of ethylene oxides.

Betaines derived from the tertiary amines represented by Formula (1) include trialkylbetaine, to describe concretely, long-chain alkyl di-lower alkylbetaines such as lauryldimethylbetaine, stearyldimethylbetaine, cocodimethylbetaine, and decyldimethylbetaine.

The following products are suitable as amine oxides derived from the tertiary amine represented by Formula (1):

(A) trialkylamine oxide

- (i) lauryldimethylamine oxide
- (ii) stearyldimethylamine oxide

(B) dihydroxyethylalkylamine oxide

- (i) dihydroxyethyloctylamine oxide
- (ii) dihydroxyethyldodecylamine oxide
- (iii) dihydroxyethyltallowamine oxide

(C) di(polyoxyethylene)alkylamine oxide

- (i) bis(polyoxyethylene)tallowamine oxide
- (ii) bis(polyoxyethylene)cocoamine oxide
- (iii) bis(polyoxyethylene)dodecylamine oxide

(D) lower alkylpolyoxyethylenealkylamine oxide

- (i) methylpolyoxyethylenecocoamine oxide.

In the present invention, the nitrogen-containing compound and oxalic acid or the specific oxalic acid salt as described above are used in combination. The salt of oxalic acid is potassium salt, alkanolamine salt, or lower alkylamine salt. The alkanolamine salt includes monoethanolamine salt, diethanolamine salt, and triethanolamine salt. The lower alkylamine salt includes monomethylamine salt, monoethylamine

salt, dimethylamine salt, and diethylamine salt. The liquid enhancer composition which is stable to a change in temperatures can not be obtained from oxalic acid salts other than the above compounds. The oxalic acid salt is preferably potassium salt or alkanolamine salt, particularly preferably potassium salt or diethanolamine salt.

Oxalic acid or the salt thereof is used in a range of 0.1 to 10 moles, preferably 0.3 to 5 moles per mole of the nitrogen-containing compound. If the amount of oxalic acid or the salt thereof is less than 0.1 mole or exceeds 10 moles, the enhancement effect of amino acid series herbicides is deteriorated, and the composition becomes unstable to a change in temperatures.

In the liquid enhancer composition of the present invention, known surfactants can be used in combination.

Nonionic surfactants, anionic surfactants, and amphoteric surfactants, or the mixture thereof can be used as the surfactants capable of being used in combination.

These surfactants can be combined at the weight

ratio of 1/1 to 1/10, preferably 1/2 to 1/6 based on the nitrogen-containing compound.

The nonionic surfactants include polyoxyethylene alkyl ether, polyoxyethylene alkylaryl ether, polyoxyethylene alkylaryl ether formaldehyde condensation product, polyoxyalkylene aryl ether, polyoxyalkylene alkyl ester, polyoxyalkylene alkylsorbitol ester, polyoxyalkylene sorbitan ester, polyoxyalkylene alkylglycerol ester, polyoxyalkylene block copolymer, polyoxyalkylene block copolymer alkylglycerol ester, polyoxyalkylene alkylsulfonamide, polyoxyalkylene rosin ester, polyoxypropylene block copolymer, polyoxyethylene oleyl ether, polyoxyalkylene alkylphenol, and the mixture of two or more kinds thereof.

Among the anionic surfactants, typical ones can be obtained in the form of an aqueous solution or a solid matter. The examples thereof include sodium mono- and di-alkylnaphthalenesulfonates, sodium alpha-olefinsulfonates, sodium alkanesulfonates, alkylsulfosuccinates, alkylsulfates, polyoxyalkylene alkyl ether sulfates, polyoxyalkylene alkylaryl ether sulfates, polyoxyalkylene styrylphenyl ether

sulfates, mono- and di- alkylbenzenesulfonates, alkylnaphthalenesulfonates, formaldehyde condensation products of alkylnaphthalenesulfonates, alkyl diphenyl ether sulfonates, olefinic sulfonates, mono- and dialkylphosphates, polyoxyalkylene mono and dialkylphosphates, polyoxyalkylene mono and diphenyl ether phosphates, polyoxyalkylene mono and diaklylphenyl ether phosphates, polycarboxylates, fatty acid salts, linear and branched alkyl polyoxyalkylene ether acetic acid or the salts thereof, alkenyl polyoxyalkylene ether acetic acid or the salts thereof, stearic acid and the salts thereof, oleic acid and the salts thereof, N-methyl fatty acid taurides, and the mixtures of two or more kinds thereof (including sodium, potassium, ammonium and amine salts).

Among these surfactants, particularly preferred are the nonionic surfactants. Of them, preferred are ester types such as polyoxyalkylene sorbitan esters and polyoxyalkylene alkylglycerol esters, polyoxyalkylene alkyl ethers, and polyoxyalkylene alkylphenyl ethers.

The liquid enhancer composition for amino acid

series herbicides of the present invention comprises the preceding nitrogen-containing compound, oxalic acid or the salt thereof, optional components blended according to necessity, and the balance of water. The form thereof is usually an aqueous solution. In the present invention, the nitrogen-containing compound is blended into the composition in a proportion of 10 to 30 weight %, preferably 15 to 25 weight %. The mole ratio of the nitrogen-containing compound to oxalic acid (salt) has to be controlled to the ratio described previously.

Further, the present invention provides a liquid herbicide composition containing the liquid enhancer composition of the present invention and the amino acid series herbicide as described above.

The amino acid series herbicide includes, for example, glyphosate (N-(phosphonomethyl)glycine or the salts thereof), bialaphos (sodium salt of L-2-amino-4-[(hydroxy)(methyl)=phosphinoyl]butyryl-L-alanyl-L-alanine), and glufosinate (ammonium-DL-homoalanine-4-yl(methyl)phosphinate).

In the liquid herbicide composition of the present invention, the ratio of the enhancer



composition of the present invention to the amino acid series herbicide is (i)/(ii)=0.05 to 50, preferably 0.05 to 20, and more preferably 0.1 to 10 in terms of a weight ratio of the total amount (i) of the nitrogen-containing compound and oxalic acid or the salt thereof contained in the enhancer composition to the agricultural chemical primary component (the active ingredient of the herbicide) (ii) contained in the amino acid series herbicide. The ratio of less than 0.05 can not sufficiently achieve the intended enhancement effect of the herbicide. Meanwhile, the ratio exceeding 50 does not allow further increase in the effect to be expected.

Further, pH regulators, inorganic salts, and thickeners may be added to the herbicide composition of the present invention according to necessity.

The pH regulator capable of being used in the present invention is citric acid, phosphoric acid (pyrophosphoric acid), gluconic acid, or the salts thereof.

The inorganic salts which can be used in the present invention include inorganic ammonium salts

such as ammonium sulfate, ammonium nitrate, ammonium phosphate, ammonium thiocyanate, ammonium chloride, and ammonium sulfamate.

The formulation of the herbicide composition of the present invention is a single liquid type (single formulation type) containing the enhancer composition and the amino acid series herbicide. It can be used as well by mixing (diluting) the amino acid series herbicide or the aqueous solution thereof with the aqueous solution of the enhancer composition immediately before using in such a proportion that the agricultural chemical concentration of the herbicide becomes the desired value.

[Examples]

The present invention shall be explained below with reference to examples but shall not be restricted to these examples.

Example 1

The nitrogen-containing compounds and oxalic acid or the salts thereof shown in Table 1 were used to obtain various liquid enhancer compositions.

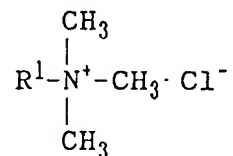
Table 1

Composi- tion No.	Nitrogen-containing compound	Oxalic acid or salt thereof	Mole* ratio	Water
1	Cocoalkyltrimethylammonium chloride	20 g		
2	Cocoalkyltrimethylammonium chloride	20 g	Oxalic acid	5.2 g
3	Cocoalkyltrimethylammonium chloride	20 g	Dipotassium oxalate	9.6 g
4	Cocoalkyltrimethylammonium chloride	20 g	Disodium oxalate	7.7 g
5	Cocoalkyltrimethylammonium chloride	20 g	Diammonium oxalate	7.2 g
6	Cocoalkyltrimethylammonium chloride	20 g	Diethanolamine oxalate	17.2 g
	Cocoalkyltrimethylammonium chloride	20 g	Dimethylamine oxalate	8.6 g
7	POE(15)beef tallow amine	20 g	Oxalic acid	5.2 g
8	POE(15)beef tallow amine	20 g	Dipotassium oxalate	9.6 g
9	POE(15)beef tallow amine	20 g	Disodium oxalate	7.7 g
10	POE(15)beef tallow amine	20 g	Diammonium oxalate	7.2 g
11	POE(15)beef tallow amine	20 g	Diethanolamine oxalate	17.2 g
12	POE(15)beef tallow amine	20 g	Dimethylamine oxalate	8.6 g
13	POE(15)cocoalkylmonomethyl- ammonium chloride	20 g	Oxalic acid	5.2 g
14	POE(15)cocoalkylmonomethyl- ammonium chloride	20 g	Dipotassium oxalate	9.6 g
15	POE(15)cocoalkylmonomethyl- ammonium chloride	20 g	Disodium oxalate	7.7 g
16	POE(15)cocoalkylmonomethyl- ammonium chloride	20 g	Diammonium oxalate	7.2 g
17	POE(15)cocoalkylmonomethyl- ammonium chloride	20 g	Diethanolamine oxalate	17.2 g
18	POE(15)cocoalkylmonomethyl- ammonium chloride	20 g	Dimethylamine oxalate	8.6 g
19	POE(2)cocoalkylmonomethyl- ammonium chloride	16 g		
	POE(6)Lauryl ether	4 g	Dipotassium oxalate	9.6 g
Comp.1	Cocoalkyltrimethylammonium chloride	20 g		
Comp.2	POE(15)beef tallow amine	20 g		
Comp.3	POE(15)cocoalkylmonomethyl- ammonium chloride	20 g		
Comp.4			Dipotassium oxalate	9.6 g
Comp.5			Diethanolamine oxalate	17.2 g

\*Mole ratio...nitrogen-containing compound: oxalic acid or salt thereof

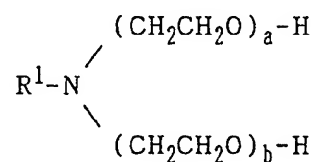
The structures of the respective nitrogen-containing compounds shown in Table 1 are as follows:

(1) Cocoalkyltrimethylammonium chloride



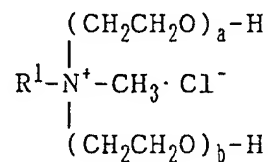
[R<sup>1</sup>: cocoalkyl]

(2) POE(15)beef tallowamine



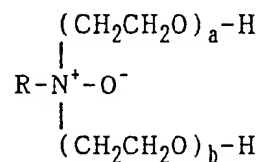
[R<sup>1</sup>: beef tallowalkyl, a + b = 15 (average)]

(3) POE(15)cocoalkylmonomethylammonium chloride



[R<sup>1</sup>: cocoalkyl, a + b = 15 (average)]

(4) BisPOE(15)tallowamine oxide



[R<sup>1</sup>: tallowalkyl, a + b = 15 (average)]

BisPOE(15)tallowamine oxide of 20 g was used to

prepare the liquid composition of total 100 g so that the mole ratio thereof to oxalic acid (salt) became 1 : 3, and the composition was evaluated in the same manner.

In order to confirm the stability with lapse of time of the compositions shown in Table 1, the compositions were stored at a high temperature (60°C), a low temperature (-5°C) and an ordinary temperature for one month. The results thereof are shown in Table 2.

Table 2

Enhancer composition No.	Storage stability		
	60°C	-5°C	ord.temp.
1	stable	stable	stable
2	stable	stable	stable
3	s.& p.	c.& p.	p.
4	s.& p.	c.& p.	p.
5	stable	stable	stable
6	stable	stable	stable
7	stable	stable	stable
8	stable	stable	stable
9	s.& p.	c.& p.	p.
10	s.& p.	c.& p.	p.
11	stable	stable	stable
12	stable	stable	stable
13	stable	stable	stable
14	stable	stable	stable
15	s.& p.	c.& p.	p.
16	s.& p.	c.& p.	p.
17	stable	stable	stable
18	stable	stable	stable
19	stable	stable	stable
Comp.1	stable	stable	stable
Comp.2	stable	stable	stable
Comp.3	stable	stable	stable
Comp.4	stable	stable	stable
Comp.5	stable	stable	stable

s.; phase separation, p.; precipitation,  
c.; cloudiness

In Table, "stable" : storage stability was good, and "precipitation, cloudiness and phase separation": change in physical properties such as precipitation, cloudiness, and phase separation was observed during a storage period of one month, and allowable storage stability was not shown.

As shown in Table 2, while the excellent temperature stability was shown when oxalic acid, dipotassium oxalate, diethanolamine oxalate, and dimethylamine oxalate were used, disodium oxalate and diammonium oxalate caused phase separation, cloudiness and precipitates to be deposited after storing at a constant temperature for one month and therefore did not provide the stable liquid enhancer compositions which were allowable in terms of the stability with lapse of time.

The compositions using bisPOE(15)tallowamine oxide also provided good stability with lapse of time when they were used in combination with oxalic acid (salts) other than disodium oxalate or diammonium oxalate.

## Example 2

The liquid enhancer compositions in Table 2 and combined with commercially available amino acid series herbicides to carry out a herbicidal efficacy test.

Used as the commercially available herbicides were a Basta (trade name) liquid formulation (containing 18.5 weight % of glufosinate as the active ingredient), a Roundup (trade name) liquid formulation (containing 41 weight % of glyphosate monoisopropylamine salt as the active ingredient), and a Herbie (trade name) liquid formulation (containing 18 weight % of Bialaphos sodium salt as the active ingredient).

The liquid enhancer compositions each were dissolved in deionized water to obtain 1 to 500-diluted liquids. And the liquid enhancer compositions having bad stability during storage dissolved in deionized water to obtain 1 to 500-diluted liquids in the same manner. The resulting 1 to 500-diluted liquids of the liquid enhancer compositions were used to further dilute each of the commercially available herbicides described above to 1 to 500. Thus, three



kinds of the liquid herbicide compositions were obtained from one enhancer composition for a liquid herbicide.

Fertile soil obtained from a paddy field, gravel (that is, river sand), and commercially available culture soil were mixed together in a weight ratio 7 : 2 : 1. The soil thus obtained was put in pots having a inner diameter of 12 cm. In order to carry out a herbicidal efficacy test in a greenhouse, the seeds of crabgrass as an example of a narrow-leaved plant and cabbage as an example of a broad-leaved plant were sowed in the pots and grown. The pots in which the plants had been abnormally grown were removed in order to eliminate unevenness by pot. The pots in which crabgrass had grown to a grass height of 20 to 30 cm and cabbage leaves had grown up to a five leaves-spreading period were subjected to the test. In order to give the herbicide compositions to the plants, the pots were put on a turntable (diameter: 36 cm) to spray the compositions by means of a spray gun (RG type, manufactured by Iwata Tosoki Kogyo Co., Ltd.).

The spray amount was adjusted to a ratio of 1000 liter/ha in case of the Basta liquid formulation and the Herbie liquid formulation, and the Roundup liquid formulation was sprayed evenly on the plants in a ratio of 500 liter/ha. Then, the herbicidal efficacies were evaluated.

The ground growth fresh weights were determined on the 14th day after spraying on the plants, and the results thereof were shown in terms of a herbicidal rate on the basis of the ground growth fresh weight of an untreated lot (refer to the following equation). Then, the herbicidal rates of the respective herbicide compositions are shown in Tables 3 and 4.

Herbicidal rate (%) = [(ground growth fresh weight (g) of the untreated lot - ground growth fresh weight (g) of the treated lot)/ground growth fresh weight (g) of the untreated lot] x 100

Table 3

Enhancer		Herbicide rate to crabgrass (%)		
composi-		Basta liquid	Roundup liquid	Herbie liquid
tion No.		formulation	formulation	formulation
Present	1	90.0	97.2	86.7
Inven-	2	90.2	95.6	89.4
tion	3	58.0	62.7	60.0
Product	4	65.2	70.5	68.4
	5	88.6	96.4	84.8
	6	87.5	93.7	89.2
	7	90.5	96.7	92.8
	8	92.4	98.6	93.8
	9	57.2	60.9	58.5
	10	66.3	65.3	63.3
	11	90.6	94.2	89.2
	12	90.0	92.3	86.4
	13	92.1	96.5	87.3
	14	93.4	98.0	90.5
	15	62.3	63.8	63.5
	16	68.5	70.2	62.5
	17	90.6	93.6	84.2
	18	86.4	94.2	86.7
	19	93.6	97.5	91.4
Comp.Ex.	1	60.5	61.5	61.2
Comp.Ex.	2	59.8	62.4	58.0
Comp.Ex.	3	60.8	63.5	62.2
Non-additive		46.7	54.2	56.0

In some cases, insoluble precipitation caused clogging of spray nozzle at spraying in the liquid enhancer compositions of No. 3, 4, 9, 10, 15, 16.

Table 4

Enhancer composi- tion No.	Herbicide rate to cabbage (%)			
	Basta liquid formulation	Roundup liquid formulation	Herbie liquid formulation	
Present	1	72.8	78.0	65.8
Inven-	2	74.8	76.4	70.2
tion	3	45.6	38.9	42.8
Product	4	50.2	40.5	49.6
	5	70.6	72.8	88.3
	6	76.2	70.8	69.1
	7	74.2	82.1	73.2
	8	78.2	80.4	74.6
	9	40.2	35.6	38.8
	10	42.5	39.5	40.6
	11	74.2	78.3	64.6
	12	72.6	74.2	68.9
	13	77.3	80.6	76.1
	14	82.2	81.6	77.4
	15	43.5	44.8	43.7
	16	46.4	48.3	47.2
	17	76.4	79.4	72.4
	18	73.2	80.2	69.3
	19	81.6	80.7	74.5
Comp. Ex. 1		43.2	35.6	42.1
Comp. Ex. 2		38.9	33.5	36.4
Comp. Ex. 3		42.6	40.1	41.8
Non-additive		35.6	20.4	24.8

In some cases, insoluble precipitation caused clogging of spray nozzle at spraying in the liquid enhancer compositions of No. 3, 4, 9, 10, 15, 16.

Among the compositions using bisPOE(15)tallowamine oxide, the compositions using oxalic acid (salt) other than disodium oxalate or diammonium oxalate showed a good herbicidal activity.

#### Example 3

Glyphosate acid (N-phosphonomethylglycine) was synthesized by a known method and neutralized with isopropylamine in order to convert it to a water soluble salt, whereby a glyphosate•isopropylamine aqueous solution (active ingredient: 70 %) was obtained.

The resulting glyphosate•isopropylamine aqueous solution and the liquid enhancer compositions for herbicides obtained in Example 1 by selecting the compositions having the stability with lapse of time (refer to Table 5) from the enhancer compositions for liquid herbicides were blended in the rates shown in Table 5, whereby the liquid herbicide compositions were obtained.

Table 5

Herbicide composition No.	Enhancer composition for liquid herbicide No.	Blend amount (g)	Glyphosate isopropylamine aqueous solution (active ingredient 70 %) blend amount (g)	Water blend amount (g)
(1)	1	37.5	58.6	3.9
(2)	2	37.5	58.6	3.9
(3)	3	37.5	58.6	3.9
(4)	4	37.5	58.6	3.9
(5)	5	37.5	58.6	3.9
(6)	6	37.5	58.6	3.9
(7)	7	37.5	58.6	3.9
(8)	8	37.5	58.6	3.9
(9)	9	37.5	58.6	3.9
(10)	10	37.5	58.6	3.9
(11)	11	37.5	58.6	3.9
(12)	12	37.5	58.6	3.9
(13)	13	37.5	58.6	3.9
(14)	14	37.5	58.6	3.9
(15)	15	37.5	58.6	3.9
(16)	16	37.5	58.6	3.9
(17)	17	37.5	58.6	3.9
(18)	18	37.5	58.6	3.9
(19)	19	37.5	58.6	3.9
(20)	Comp. Ex. 1	37.5	58.6	3.9
(21)	Comp. Ex. 2	37.5	58.6	3.9
(22)	Comp. Ex. 3	37.5	58.6	3.9
(23)	Comp. Ex. 4	37.5	58.6	3.9
(24)	Comp. Ex. 5	37.5	58.6	3.9

The liquid compositions using bisPOE(15)tallowamine oxide were prepared and evaluated in the same manners.

The herbicide compositions shown in Table 5 were stored at a high temperature (60°C), a low temperature (-5°C) and an ordinary temperature for one month in order to confirm the stability with lapse of time thereof. The results thereof are shown in Table 6.



Table 6

Herbicide composition No.	Storage stability		
	60°C	-5°C	ord.temp.
1	stable	stable	stable
2	stable	stable	stable
3	s.& p.	c.& p.	c.& p.
4	s.& p.	c.& p.	c.& p.
5	stable	stable	stable
6	stable	stable	stable
7	stable	stable	stable
8	stable	stable	stable
9	s.& p.	c.& p.	c.& p.
10	s.& p.	c.& p.	c.& p.
11	stable	stable	stable
12	stable	stable	stable
13	stable	stable	stable
14	stable	stable	stable
15	s.& p.	c.& p.	c.& p.
16	s.& p.	c.& p.	c.& p.
17	stable	stable	stable
18	stable	stable	stable
19	stable	stable	stable
20	stable	stable	stable
21	stable	stable	stable
22	stable	stable	stable
23	stable	stable	stable
24	stable	stable	stable

s.; phase separation, p.; precipitation,  
c.; cloudiness

As shown in Table 6, the liquid herbicide compositions using the enhancers for liquid herbicides of the present invention were stable to a change in temperatures with lapse of time.

The compositions using bisPOE(15)tallowamine oxide other than disodium oxalate or diammonium oxalate provided a good storage stability as well.

Example 4

Various liquid herbicide compositions shown in Table 6 in Example 3 were used to carry out the following herbicidal efficacy test.

First, the liquid herbicide compositions each were diluted to 1 to 300 with deionized water to obtain spray liquids.

Fertile soil obtained from a paddy field, gravel (that is, river sand), and commercially available culture soil were mixed together in a weight ratio 7 : 2 : 1. The soil thus obtained was put in a pot having a inner diameter of 12 cm. In order to carry out the herbicidal efficacy test in a greenhouse, the seeds of crabgrass as an example of a narrow-leaved plant and cabbage as an example of a broad-leaved

plant were sowed in the pots and grown. The pots in which the plants had been abnormally grown were removed in order to eliminate unevenness by pot. The pots in which crabgrass had grown to a grass height of 20 to 30 cm and cabbage leaves had grown up to a five leaves-spreading period were subjected to the test. In order to give the herbicide compositions to the plants, the pots were put on a turntable (diameter: 36 cm) to spray the compositions by means of a spray gun (RG type, manufactured by Iwata Tosoki Kogyo Co., Ltd.). The compositions were sprayed evenly on the plants in an amount corresponding to a ratio of 500 liter/ha, and the herbicidal efficacies were evaluated.

The ground growth fresh weights were determined on the 14th day after spraying on the plants, and the results thereof were shown in terms of a herbicidal rate on the basis of the ground growth fresh weight of an untreated lot (refer to the following equation). The herbicidal rates of the respective herbicide compositions are shown in Table 7.

Herbicidal rate (%) = [(ground growth fresh weight  
(g) of the untreated lot - ground growth fresh weight  
(g) of the treated lot)/ground growth fresh weight  
(g) of the untreated lot] x 100

Table 7

Herbicide composition No.	Herbicidal rate to crabgrass (%)	Herbicidal rate to cabbage (%)
1	93.2	62.4
2	90.2	85.2
3	62.6	33.4
4	64.1	35.1
5	88.5	59.8
6	85.3	61.8
7	92.5	68.4
8	88.7	73.1
9	60.8	31.3
10	65.3	33.3
11	85.6	70.5
12	87.3	66
13	90.6	71.8
14	93.4	75.3
15	65.3	34.1
16	67.2	35.6
17	86.5	70.4
18	82.7	68.7
19	91.7	72.1
20	60.5	28.3
21	60.4	29.5
22	61.8	30.4
23	54.6	25.4
24	58.3	26.3
Roundup liquid formulation	62.3	30.5

In some cases, insoluble precipitation caused clogging of spray nozzle at spraying in the liquid enhancer compositions of No. 3, 4, 9, 10, 15, 16.

The compositions using bisPOE(15)tallowamine oxide other than disodium oxalate or diammonium oxalate showed a good herbicidal activity as well.

## Claims

1. A liquid enhancer composition for herbicides of amino acid compounds which comprises (1) at least one nitrogen-containing compound selected from tertiary amine compounds represented by the following Formula (1) and derivatives thereof, and (2) at least one oxalic acid compound selected from the group consisting of oxalic acid, potassium oxalate, alkanolamine salts of oxalic acid and lower alkylamine salts of oxalic acid, at a mole ratio of (2) the oxalic acid compound to (1) the nitrogen-containing compound ranging between 0.1/1 and 10/1:



[wherein

$\text{R}^1$ : represents a linear or branched alkyl group having the carbon number of 8 to 30 or a linear or branched alkenyl group having the carbon number of 8 to 30, and

$\text{R}^2$ ,  $\text{R}^3$ : may be the same as or different from each other and each represent a linear or branched alkyl

group having the carbon number of 1 to 30, a linear or branched alkenyl group having the carbon number of 2 to 30, or  $-(AO)_n-H$  (AO is an oxyalkylene group having the carbon number of 2 to 4, and n is a number of 1 to 30 on the average.))]

2. The enhancer composition as claimed in Claim 1, in which the derivative is selected from the group consisting of amine salts, quaternized products, betaines and amine oxides of the tertiary amine compound represented by Formula (1).

3. The enhancer composition as claimed in Claim 1, which further comprises a surfactant.

4. An aqueous solution of the composition as claimed in Claim 1, comprising 10 to 30 percent by weight of the nitrogen-containing compound.

5. An herbicide composition comprising (i) an effective amount of at least one nitrogen-containing compound as defined in Claim 1 and an effective amount of the oxalic acid compound as defined in Claim 1 and (ii) a herbicide of amino acid compound.

6. The herbicide composition as claimed in Claim 5, in which the herbicide is selected from the



group consisting of glyphosate (N-(phosphonomethyl)-glycine, salts thereof), bialaphos (sodium salt of L-2-amino-4-[(hydroxy)(methyl)=phosphinoyl]butyryl-L-alanyl-L-alanine) and glufosinate (ammonium-DL-homoalanine-4-yl(methyl)phosphinate).

7. The herbicide composition as claimed in Claim 5, in which a weight ratio of (i) to (ii) ranges from 0.05/1 to 50/1.

8. A method for enhancing the herbicidal effectiveness of (ii) a herbicide of amino acid compound with (i) an effective amount of at least one nitrogen-containing compound as defined in Claim 1 and an effective amount of the oxalic acid compound as defined in Claim 1.

## INTERNATIONAL SEARCH REPORT

International Application No

PC., JP 96/01781

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 A01N57/20

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	W0,A,95 17817 (KAO CORPORATION) 6 July 1995 cited in the application see claims 1,2 see page 37, line 4 - line 6 see table 4 see page 56, line 15-21 ---	1-8
X	RESEARCH DISCLOSURE, no. 15334, January 1977, HAVANT GB, XP002018087 "Herbicide compositions containing N-phosphonomethyl glycines" see page 35 - page 36 -----	1-8

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+31-70) 340-3016

Authorized officer

Fort, M

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/JP 96/01781

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9517817	06-07-95	BR-A- 9406470	23-01-96
		CN-A- 1118567	13-03-96
		EP-A- 0685995	13-12-95
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